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THE CONTENT OF CADMIUM IN HONEY FROM THE REPUBLIC OF MACEDONIA

Elena STANKOVSKA[1], Trajče STAFILOV[1]* and Robert ŠAJN[2]

Institute of Chemistry, Faculty of Science, Sts. Cyril and Methodius University, PO Box 162, 1000 Skopje, Macedonia
Geological Survey of Slovenia, Dimičeva ul. 14, 1000 Ljubljana, Slovenia

ABSTRACT

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The content of cadmium in 123 honey samples collected from different parts of the Republic of Macedonia was determined by electrothermal atomic absorption spectrometry. The microwave digestion system was applied for digestion of the samples. It was found that the content of cadmium varies from below detection limit (1.0 μg kg^{-1}) to 267.9 μg kg^{-1} with the mean content of 3.63 μg kg^{-1}. The highest content of Cd was found in the honey samples from the central part of Macedonia (region of Veles) in connection to the existence of lead, zinc and cadmium smelter plant in this region. Mean value of Cd in honey samples from the region of Veles is three times higher than the determined mean for Macedonia. Relatively high contents are also found in the eastern part of Macedonia which is a consequence of natural enrichment of Cd with the geological formations associated with Pb-Zn mines Sasa and Toranica.

Keywords: Honey, Trace elements, Microwave digestion, Atomic absorption spectrometry

ИЗВОД

Станковска, Е., Стафилов, Т., Шајн, Р. (2006/2007) Содржина на кадмиум во мед од Република Македонија. Екол. Зашт. Живот. Сред., Том 10, Бр. 1-2, 11-17, Скопје.

Определена е содржината на кадмиум во 123 примероци од мед земени од различни региони во Република Македонија со примена на електротермичката атомска апсорпциона спектрометрија. Примероците се разложени со помош на микробранов систем. Утврдено е дека содржината на кадмиумот се движи од границата на детекција на методот (1.0 μg kg^{-1}) до 267.9 μg kg^{-1}, при што средната вредност изнесува 3.63 μg kg^{-1}. Највисоки вредности за содржината на кадмиум се најдени во примероците од мед од централниот дел на Македонија што е како резултат на работата на Топилницата за олово, цинк и кадмиум во Велес. Средната вредност за содржината на кадмиум во примероците од овој регион е за три пати повисока од онаа за Македонија. Релативно високи содржини се најдени и во примероци од источниот дел на Македонија што може да се поврзе со природно зголемената содржина на кадмиум во геолошките формации во овој регион (рудници за олово и цинк Саса и Тораница).

Клучни зборови: мед, елементи во трагови, микробраново разложување, атомска апсорпциона спектрометрија

*Corresponding author. Tel.: +389 2 3249906; fax: +389 2 3226 865; E-mail address: trajcest@iunona.pmf.ukim.edu.mk

Introduction

Honey is produced from the plant nectar, as well as from honeydew, which bees collect, process and place into honey combs. Honey contains mainly carbohydrates (mainly fructose and glucose, and also in small content maltose and saccaharose) and water. Mineral content in honey varies from 0.04 % in pale to 0.2 % in dark honeys (Anklam, 1998). Among other components in honey, some traces of proteins and enzymes, amino acids, pigments, substances which give flavor and aroma, plant acids, alcohols and vitamins, are also present. Today the use of honey is widespread and not only because of its nutritional value, content of vitamins, essential elements, antioxidant substances but also due to its antibacterial, antimutagene and probiotic characteristics (Arvanitoyannis et al., 2005).

The content of the elements in honey depends on the soil composition on which the plants grow, and also according to the botanical origin of the plant from which bees take nectar (Matei et al., 2004). It is also known that the content of some heavy metals (including cadmium) in honey could be a result of anthropogenic contamination (Przybylowsky and, 2001; Tuzen and Soylak, 2005). The presence of cadmium in the environment is mainly because of the emission from the process of cadmium production and manufacture of cadmium products (batteries, pigments and coatings). Cadmium is recognized to produce toxic effects on humans (Casarett & Doull's Toxicology 1995).

Atomic absorption spectrometry (AAS) has frequently been used in analysis of heavy metals in honey. Due to very low content in honey, cadmium is determined by electrothermal atomic absorption spectrometry - ETAAS (Gonzales Paramas et al., 2000; Conti and Botre, 2001; Przybylowsky & Wilczyńska, 2001; Vorlova and Čelechovska, 2002; Tadia et al., 2004; Rashed and Soltan, 2004; Atrouse et al., 2004; Erbilir and Erdoğrul, 2005, Tuzen and Soylak, 2005).

It is known that honey could be very useful biomonitor for heavy metals (Przybylowsky and Wilczyńska 2001; Tuzen and Soylak 2005; Bogdanov 2006). Therefore, in this work cadmium content was determined in 123 honey samples collected from 12 regions of the Republic of Macedonia. The aim is to contribute to the scarce data about the mineral content of Macedonian honey and to investigate possible anthropogenetic influence on cadmium content in honey by the regions in Macedonia.

Materials and methods

Apparatus

The measurements were performed using Varian SpectrAA 640Z atomic absorption spectrometer with Zeeman corrector, equipped with electrothermal atomizer GTA 100 and autosampler Varian PSD 100. As a source, hallow cathode lamp was used. The optimal instrumental parameters are given in Tab. 1.

Tab. 1. Instrumental parameters for determination of Cd by ETAAS
Таб. 1 Вредности на параметрите при определувањето на Cd со ETAAS

Parameters/Параметри	**Cd**
Wavelength/nm	228.8 nm
Slit width/nm	0.5 nm
Lamp current/mA	4 mA
Calibration mode	Absorbance, peak height
Background correction	Zeeman
Drying	
Temperature	95 ^{o}C
Ramp time	40 s
Hold time	10 s
Ashing	
Temperature/^{o}C	250 ^{o}C
Ramp time/s	10 s
Hold time/s	15 s
Atomization	
Temperature/^{o}C	1800 ^{o}C
Ramp time/s	0.8 s
Hold time/s	2 s
Cleaning	
Temperature/^{o}C	1800 ^{o}C
Ramp time/s	2 s
Hold time/s	2 s
Gas	Argon

Reagents and samples

All reagents and standard solutions were *p.a.* grade. Redistilled water was used for the preparation of all solutions. Stock standard solution with a concentration of 1000 mg L^{-1} for Cd was manufactured by Solution Plus Inc. (USA).
A total of 123 samples were collected from individual bee keepers all over the territory of

the Republic of Macedonia (Fig. 1). The samples were collected from 12 regions in the country. About 250 g of each sample were placed in plastic bottles and kept in a dry and clean place until the analysis.

Sample preparation

In order the effects of the organic matrix to be minimized, microwave assisted sample digestion was performed prior analysis. Milestone Ethos Touch Control medium pressure microwave digestion system was used.

Approximately 0.5 g of honey was placed into PTFE vessels and 2 ml of concentrated HNO_3 and 2 ml of H_2O_2 (30%, *m/V*) were added. The vessels were capped closed, tightened and placed in the rotor of microwave oven and digested with the two step procedure given in Tab. 2. Ventilation was performed for 20 minutes after the end of the second step. Finally the vessels were cooled, carefully opened and quantitatively transferred in 50 ml calibrated flasks.

Fig. 1. Sketch map of researched areas with sampling locations
Сл. 1 Шематска карта на истражуваните подрачја со локалитети од каде се земани проби

Tab. 2 Procedure used for the digestion of honey samples
Таб. 2 Користена процедура при согорувањето на примероците мед

Step Фаза	Temperature/°C Температура	Time/min Време	Power/W Моќност	Pressure/bar Притисок
1	180	5	500	20
2	180	10	500	20

Results and discussion

Food is the main source of cadmium intake for non-occupationally exposed people. Crops grown in polluted soil or irrigated with polluted water may contain increased concentrations of cadmium (Bogdanov, 2006). Kidneys and livers concentrate cadmium (Casarett & Doull's Toxicology, 1995; World Health Organization, 1992, 2004). Levels in fruit, meat and vegetables are usually below 10 µg

kg^{-1}. Average daily intakes from food in non-contaminated areas is at the lower end of the 10 to 25 µg range of which approximately 0.5 to 1.0 µg is actually retained in the body. Uptake of cadmium from smoking could more than double that amount. More recently, the possible role of cadmium in human carcinogenesis has also been studied in some detail (Casarett & Doull's Toxicology 1995; World Health Organization 1992, 2004).

Therefore, it is very important to analyze the content of Cd in honey samples in terms of its toxicity, as well as the fact that Cd can be transported trough the root system into the nectar of the plants (Bogdanov 2006). Honey could be also used as a biomonitor for cadmium contamination of the environment (Przybylowsky and Wilczyńska 2001; Tuzen and Soylak 2005; Bogdanov 2006).

The results obtained for the content of Cd in honey samples from different regions from the Republic of Macedonia, determined by ETAAS (previously digested by microwave digestion system) are given in Tables 3. In this table the mean content for each location, as well as the median, minimum and the maximum value are given.

The maximum permitted value for Cd in honey in Macedonian legislation is set to be 30 µg kg^{-1}. Only 6 out of 123 samples in total had Cd content higher than 30 µg kg^{-1} and only one much higher content of 267.9 µg kg^{-1}. The highest mean content of Cd was detected for Veles region, being 11.28 µg kg^{-1}. In 55 samples the Cd content was below the detection limit of the method (1.0 µg kg^{-1}).

The distribution of Cd in Macedonia is influenced mainly by the anthropogenic activities. The highest contents of Cd are concentrated in the central part of Macedonia (region of Veles) in connection to the existence of lead, zinc and cadmium smelter plant in this region (Fig. 1). Mean of Cd, in Veles region is three times higher than determined mean for Macedonia (Tables 3). Relatively high concentrations are also found in the eastern part of Macedonia (Berovo and Strumica regions) which are consequences of natural enrichment of Cd on an outcrops of Neogene dacite-andesites and pyroclastites. On that geological formations are associated Pb-Zn mines Sasa and Toranica.

Tab. 3. Content of Cd in honey samples from 12 different regions (µg kg^{-1}).
Таб. 3 Содржина на Cd во примероците од мед од 12 различни регион (µg kg^{-1}).

Region (No. of samples) Регион (број примероци)	**Range** Опсег	**Geometric Mean** Геометриска средина	**Median** Медијана	**Geometric mean/ Geometric mean for Macedonia** Геометриска средина/ Геометриска средина за Македонија
Berovo (5)	1.43-67.71	9.50	11.14	2.615
Bitola (5)	< 1.0-6.20	1.96	1.99	0.540
Gostivar (9)	<1.0-6.87	2.06	1.36	0.569
Kičevo (6)	<1.0-6.29	1.72	1.0	0.474
Kumanovo (21)	< 1.0-16.21	3.09	3.06	0.850
Ohrid (5)	<1.0-32.58	3.92	1.0	1.080
Prilep (14)	<1.0-267.9	6.32	6.50	1.741
Probištip (10)	<1.0-22.68	2.34	1.0	0.644
Skopje (15)	<1.0.-38.19	2.65	1.0	0.729
Štip (13)	<1.0-18.96	1.68	1.0	0.463
Strumica (6)	5.26-27.70	10.50	10.77	2.892
Veles (14)	<1.0-55.27	11.28	12.45	3.107
Macedonia (123)	<1.0-267.9	3.63	3.06	-

It is obvious that the emission from the lead and zinc smelter plant influence on the cadmium content in honey samples from Veles region which confirms previous data about the high content of Cd in soil and some vegetable and fruit products (Stafilov, et al., 1994; Jordanovska and Stafilov 1996; Stafilov and Jordanovska 1997; Filipovski 2003; Pančevski and Stafilov 2006, 2007; Stafilov and Kulevanova 1994; Panovska et al., 1997).

The obtained mean values for Cd content in honey collected from Macedonia, as well as the content range, are similiar to those found for honey samples non-contaminated

regions: Middle Anatolia, Turkey (Tuzen and Soylak 2005), Spain (González Paramás et al. 2000; Terrab et al. 2004; González-Miret et al. 2005). However, data for honey from the Veles, Berovo and Strumica are comerable to literature data for simillar regions in Europe (France, Devillers et al. 2002; Pomeranian region, Poland, Przybylowski & Wilczyńska 2001 or from Czech Republic, Čelechovská & Vorlová 2001).

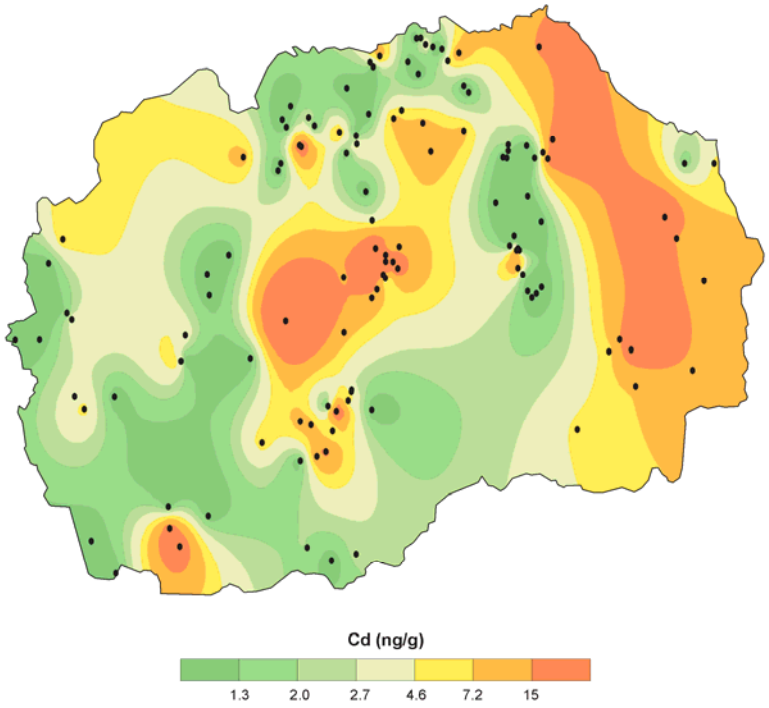

Fig. 2. Areal distribution of Cd in Macedonian honey
Сл. 2 Содржина на Cd во медот по региони во Македонија

Conclusions

In this work the content of cadmium in 123 honey samples from the Republic of Macedonia was determined by microwave digestion and electrothermal atomic absorption spectrometry. It was found that the mean contents obtained, varied from below detection limit (1 μg kg^{-1}) to 11.28 μg kg^{-1} for Veles region. The maximum permitted value for Cd in honey in Macedonian legislation is set to be 30 μg kg^{-1}. Only 6 out of 123 samples in total had Cd content higher than 30 μg kg^{-1} and only one much higher content of 267.9 μg kg^{-1}. The distribution of Cd in Macedonia is influenced mainly by anthropogenic activities. The highest content of Cd was found in the honey samples from the central part of Macedonia (region of Veles) in connection to the existence of lead, zinc and cadmium smelter plant in this region. Relatively high concentrations are also found in the eastern part of Macedonia (Berovo and Strumica regions) which are consequences of natural enrichment of Cd with the geological formations associated with Pb-Zn mines Sasa and Toranica.

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СОДРЖИНА НА КАДМИУМ ВО МЕД ОД РЕПУБЛИКА МАКЕДОНИЈА

Елена СТАНКОВСКА[1], Трајче СТАФИЛОВ[1], Роберт ШАЈН[2]

[1]Институт за хемија, Природно-математички факултет, п. фах 162, 1000 Скопје, Македонија
[2]Геолошки завод, Димиќева 14, 1000 Љубљана, Словенија

Резиме

Определена е содржината на кадмиум во 123 примероци од мед земени од различни региони во Република Македонија со примена на електротермичката атомска апсорпциона спектрометрија. Примероците се разложени со помош на микробранов систем. Утврдено е дека содржината на кадмиумот се движи од границата на детекција на методата (1.0 μg kg^{-1}) до 267.9 μg kg^{-1}, при што средната вредност изнесува 3.63 μg kg^{-1}. Покажано е дека на дистрибуцијата на кадмиум во Македонија најголемо влијание имаат антропогените активности. Така, највисоки вредности за содржината на кадмиум се најдени во примероците од мед од централниот дел на Македонија што е како резултат на работата на Топилницата за олово, цинк и кадмиум во Велес. Средната вредност за содржината на кадмиум во примероците од овој регион е за три пати повисока од онаа за Македонија. Релативно високи содржини се најдени и во примероци од источниот дел на Македонија што може да се поврзе со природно зголемената содржина на кадмиум во геолошките формации во овој регион (рудници за олово и цинк Саса и Тораница).

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